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Quarterly Technical Summary Report No. 4

September 1, 1966 to November 30, 1966

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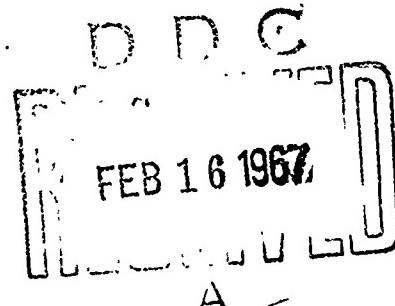
RESEARCH ON THE DEFLAGRATION
OF HIGH-ENERGY SOLID OXIDIZERS

Contract No. AF 49(638)-1645

To:

Air Force Office of Scientific Research
Washington, D. C.

December 30, 1966



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RESEARCH ON THE DEFLAGRATION
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To:

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Washington, D. C.

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December 30, 1966

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I. ABSTRACT AND INTRODUCTION

During the quarter work was initiated on two new tasks of the program. One of these is the study of the self-deflagration of hydroxyl-ammonium perchlorate (HAP), and the second is an investigation of solid-oxidizer and propellant extinguishment. The effort to present has principally been devoted to design and construction of apparatus, preliminary calculations and acquiring and analyzing HAP. Progress along these lines is outlined below.

The chief investigator attended the 3rd ICRPG Combustion Conference at Cape Kennedy on October 17-21 and presented a talk at the Propellant Ingredient Decomposition session.

II. PRELIMINARY WORK ON HYDROXYLAMMONIUM PERCHLORATE (HAP).

Previous studies in this laboratory on the self-deflagration of solid oxidizers were carried out on ammonium perchlorate (AP), hydrazine perchlorate (HP), and hydrazine diperchlorate (HDP). These were performed under the present contract or under previous contracts with AFOSR. The program is continuing and HAP has been selected as the next oxidizer candidate. The choice of HAP was made because of its potential use as a practical propellant ingredient; because it is a perchlorate-based oxidizer which should allow meaningful comparison with previously studied compounds; and because its thermal decomposition has been reported⁽¹⁾, which is an important component in understanding the deflagration.

Some selected properties of HAP are listed for reference in Table I. For deflagration considerations, the low melting point of 85°C is significant. Presumably it will burn with a deep liquid layer. It is known from the work on HP and HDP, which also enter the deflagration wave as liquids, that a molten surface layer is very conducive to condensed-phase chemical reaction.

TABLE I

Properties of Hydroxylammonium Perchlorate

Molecular Weight	133.5
Melting Point	85°C
Crystal Density	2.06 g/cc
Hygroscopicity *	5.6% Relative Humidity
Heat of Formation	-66.5 K cal/mole
Heat of Sublimation	33 K cal/mole (?)
Vapor Pressure	10^{-5} Torr at 95°C 10^{-2} Torr at 160°C } (?)

HAP is a white, monoclinic solid of chemical formula $\text{HONH}_3^+ \text{ClO}_4^-$. It decomposes at a measurable rate above 120°C to H_2O , O_2 , N_2 , N_2O , Cl_2 , HCl , H_2 , and probably small amounts of AP. DTA shows a melting endotherm at 85°C and a strong exotherm at ~ 200°C. Apparently, for laboratory purposes, it is only slightly more hazardous than AP.

* Defined by the supplier, Thiokol Elkton Division, as the point at which sample first absorbs moisture at ambient temperature.

A supply of HAP which was on hand was assayed prior to use. Chloride analysis of this material indicated a purity of approximately 60 per cent. Presumably adsorbed H_2O was the cause of this low assay, but in lieu of reclaiming dry HAP, fresh material was obtained from Thiokol Elkton Division. Analysis of this new supply is presently being carried out.

We have performed flame temperature calculations for HAP using an IBM 7090 computer and these are shown in Table II. An adiabatic, constant pressure process was assumed and an initial temperature of $25^{\circ}C$ was taken. A standard heat of formation of -66.5 K cal/mole was used⁽²⁾. For comparison, the calculated flame temperatures reported by Friedman et al.⁽³⁾ for the self-deflagration of AP are 1410 and $1440^{\circ}K$ at 1 and 100 atm, respectively.

The low product-gas temperature will allow the calculated theoretical value to be compared with measurements of the actual temperature using fine thermocouples. These experiments are planned for the future along with temperature profile measurements and the determination of the pressure dependence of the deflagration rate. Further experiments as seem necessary are also expected to be conducted. To date we can only report that we have been unable to ignite the 60 per cent pure HAP at ambient pressure. Fuel-assisted deflagrations have been obtained at 1 atm, and comparison of these with similar AP burnings indicates that the low-melting-point character of HAP promotes deflagration. This seems to be due to enhanced condensed-phase mixing caused by the wettability of the solid fuel and its capillary action on the liquid oxidizer. These preliminary findings may require further investigation as they indicate that important phenomena may be being overlooked in composite propellant deflagration. There are definite implications present that the meltability and wettability of oxidizer and/or binder and their viscosity may have principal roles on a microscale in the deflagration process. Some knowledge in this area could lead to improved control of the ignition and burning of composites.

Finally it is apparent that the extreme hygroscopicity of HAP is going to be a major problem in the program and may cause limitations.

TABLE II

Calculated Adiabatic Constant Pressure Product-Gas Temperature
and Composition for HAP Self-Deflagration.

$$\begin{array}{lll} P = 1 \text{ atm} & P = 10 \text{ atm} & P = 100 \text{ atm} \\ T_f = 1365^\circ\text{K} & T_f = 1376^\circ\text{K} & T_f = 1394^\circ\text{K} \end{array}$$

Species

Cl	6.50×10^{-3}	3.63×10^{-3}	1.960×10^{-3}
H ₂ O	1.521	2.14	1.606
HC1	.959	.904	.793
O ₂	1.740	1.729	1.699
OH	2.19×10^{-4}	1.385×10^{-4}	$.955 \times 10^{-4}$
N ₂	.500	.500	.500
NO	1.470×10^{-3}	1.558×10^{-3}	1.719×10^{-3}
NO ₂	1.598×10^{-5}	5.14×10^{-5}	1.665×10^{-4}
Cl ₂	1.790×10^{-2}	4.72×10^{-2}	1.030×10^{-1}

Initial temperature = 25°C; $\Delta H_f^\circ = -66.5$ K cal/mole. Concentrations of product species given in moles/mole HAP; any species not shown is $< 10^{-5}$.

At 18 per cent relative humidity, for example, crystalline HAP absorbs enough moisture to nearly dissolve itself within 10 minutes. Very special handling will be required.

III. DESIGN OF BURNER FOR EXTINGUISHMENT STUDIES.

An Atlantic Research Corporation Optical Bomb is to be modified to provide a means for rapidly venting pressure during strand burning, and for simultaneously measuring pressure decay rates and light emission from the burning strand. A Kistler pressure transducer connected directly to the bomb body and a phototube positioned at one of the fused-silica windows will be used to accomplish the last two measurements. Output from these sensors will be fed to a dual-trace oscilloscope where the display can be photographed. Appropriate triggering, timers and amplifiers will be required. Using the light emission as a measure of combustion rate, the extinction point will be identifiable. This in turn will correspond to a critical pressure-decay rate recorded simultaneously. These measurements then will yield the required data for understanding quenching phenomena and for testing theories of response of combustion to pressure transients⁽⁴⁾.

The key to obtaining reliable experimental data is proper design of a ventable bomb. A sketch (not to scale) of the essential features of the head block for a modified Atlantic Research Corporation optical bomb is shown in Figure 1. Plans have been drawn and a block will be machined in the near future. Following is a description of the working of the bomb.

A strand of propellant or oxidizer is mounted on a stage supported by posts which are connected to the head. With the head in position in the bomb body, the apparatus is pressurized with nitrogen. The strand is ignited electrically by a hot wire led in through the head (not shown in the figure). After steady-state burning is reached the solenoid-driven plunger is activated which bursts the rupture diaphragm. Rapid depressurization ensues with accompanying extinguishment of the strand. Measurements are made of pressure fall and light emission as previously described. Pressure decay rates can

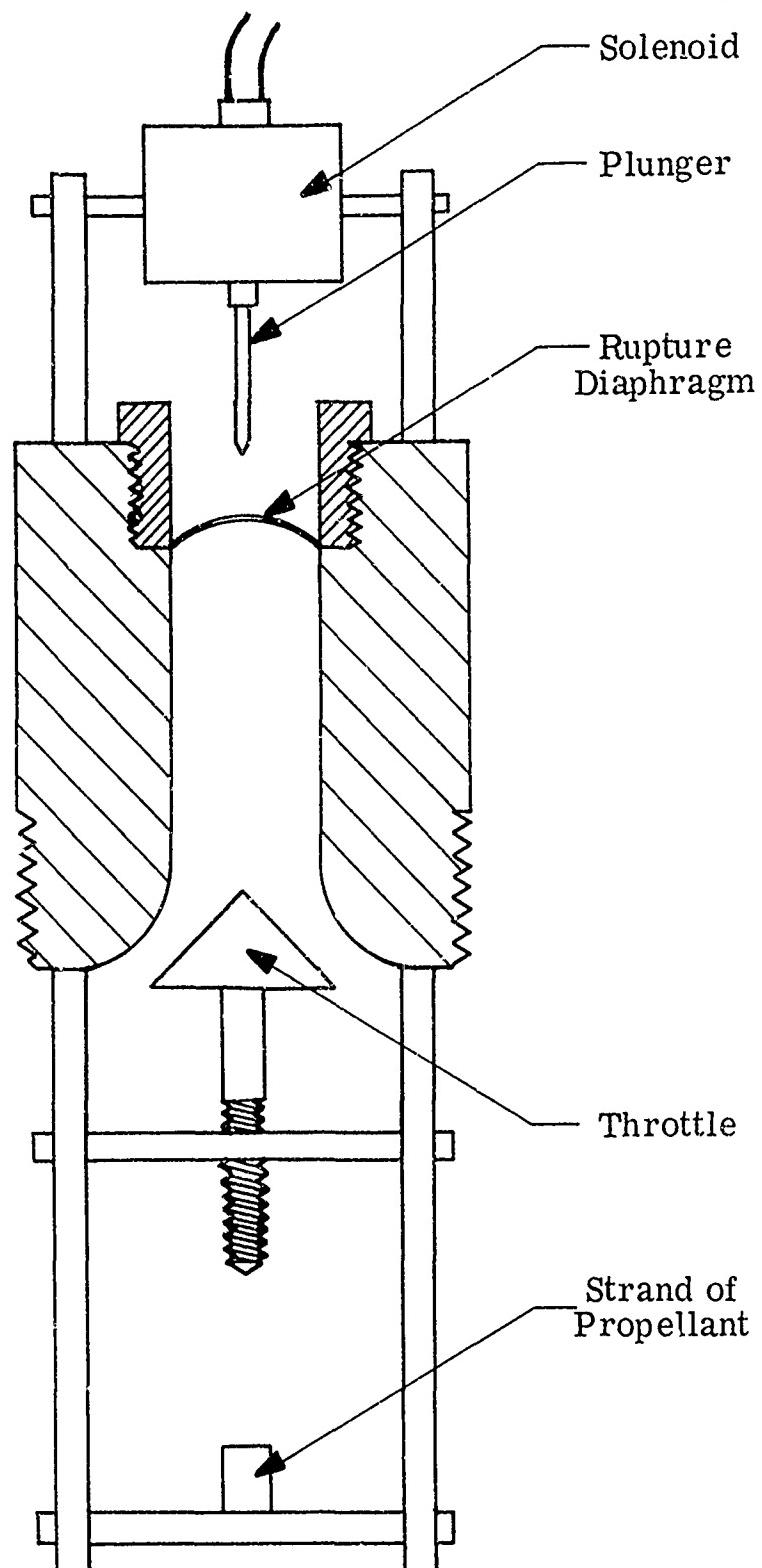


Figure 1. Optical Bomb Head Block with Nozzle
for Study of Extinguishment of Solid
Propellants.

be varied by adjusting the position of the wedge-like throttle in the throat of the one-inch nozzle. The rarefaction wave will remain in the nozzle and the pressure should be virtually constant throughout the bomb at any instant.

For this method, pressure decay rates are given to a close approximation by

$$\frac{dp}{dt} = CP,$$

where C is a function of the nozzle throat area, the volume of the bomb chamber, and the thermodynamic properties of the chamber gas⁽⁵⁾. Taking a bomb of 30 cubic inches internal volume and a speed of sound of 13,000 in/sec in the chamber gas, one calculates $C = 200 \text{ sec}^{-1}$ for a one-inch nozzle. Hence, at a pressure of 1000 psi, for example, $\frac{dp}{dt} = 200,000 \text{ psi/sec}$. Rates as high as this should be adequate for quenching studies^(4,6), and will permit a wide range of pressures and propellant compositions to be investigated.

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13. ABSTRACT

During the quarter work was initiated on two new tasks of the program. One of these is the study of the self-deflagration of hydroxylammonium perchlorate (HAP), and the second is an investigation of solid-oxidizer and propellant extinguishment. The effort to present has principally been devoted to design and construction of apparatus, preliminary calculations and acquiring and analyzing HAP. Progress along these lines is outlined.

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